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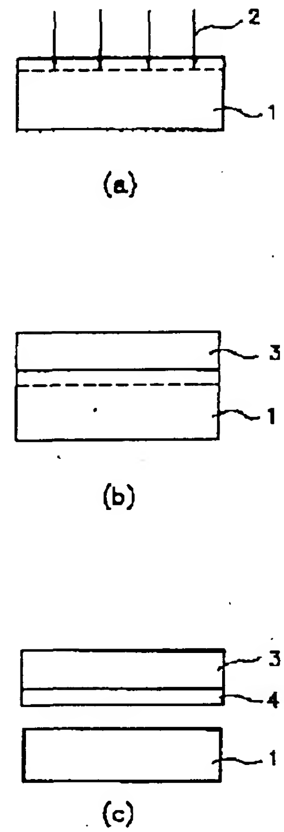

PUBLICATION NUMBER : 10093122
PUBLICATION DATE : 10-04-98

APPLICATION DATE : 10-09-96
APPLICATION NUMBER : 08239445

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INT.CL. : H01L 31/04 C30B 29/06 C30B 31/22 H01L 21/265

TITLE : METHOD OF MANUFACTURING THIN-FILM SOLAR CELL

ABSTRACT : PROBLEM TO BE SOLVED: To inexpensively manufacture a thin-film solar cell, having a const. photoelectric conversion efficiency with reduced Si consumption.

SOLUTION: An Si substrate 1, made from a single crystal or very large grain size type polycrystalline ingot or a wafer is implanted with H ions 2, second substrate 3 is adhered onto it, an suitable heat treatment is applied to peel thin film Si crystals 4 of desired thickness from the Si substrate 1 at the ion-implanted part so as to provide a major material or part thereof for composing solar cell elements.

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of the thin film solar cell constituted by the silicon (Si) thin film by which the laminating was carried out on the substrate.
[0002]
[Problem(s) to be Solved by the Invention] The thin film Si solar battery with little [using Si semiconductor with the high conversion efficiency from sunlight to the electrical and electric equipment] material resources consumption which is structure is important as one of the bearers of an energy need by whom much more increase will be expected from now on. Since the optical-absorption coefficient of Si material in a sunlight spectrum was small, in order to have manufactured the solar battery which maintained the fixed photoelectric conversion efficiency in the conventional thin film Si solar battery, about 70 microns was required also of the minimum as Si thickness.
[0003] however, with the fast spread of the photovoltaics expected, we are anxious about the need of Si which is the principal component of cell material becoming huge, and the solar-battery structure which suppressed use of Si material from the request like resources to the minimum (namely, -- most -- direct -- Si thickness -- the minimum -- carrying out), and maintained the fixed photoelectric conversion efficiency will be demanded in the future
[0004] There were some which cut down the thinnest possible Si wafer (it slices), or perform various known processings succeedingly required for solar-battery formation as a method of manufacturing such a saving-resources type Si solar battery, through the process which deposits Si thin film layer on a [2] predetermined substrate from the bulk crystal (the so-called ingot) of [1] single crystal or a polycrystal.
[0005]
[Problem(s) to be Solved by the Invention] However, in the case of the method of the above [1], the problem was in the homogeneity of the thickness of Si wafer to cut down. Moreover, when it was going to secure the fixed manufacture yield from the mechanical strength of a wafer, and the problem of workability in the process which pastes up the cut-down wafer on a certain substrate, about 100-micron thickness was needed and the minimum had also stopped at thickness inadequate for the request of saving resources. Moreover, the amount of Si used as the scraps in the case of logging also had the problem that it could not ignore as compared with thickness.
[0006] Moreover, although it was going to obtain the comparatively efficient solar battery by the various methods of making heat treatment etc. the start by the method of the above [2] to the amorphous or small polycrystal Si thin film of particle size beforehand deposited on the substrate nothing [of the diameter of crystal grain / large Si thin film and nothing / large], and this In this case, acquisition of desired thickness (for example, 10 microns) had the relatively large cost which a long time or hot heat treatment required for operation of this method of a possible thing etc. takes, and had become a practical problem.
[0007] the case where glass cheap further again in order to press down a manufacturing cost etc. is chosen as a substrate -- from a heat-resistant problem -- comparatively -- heat treatment of low temperature or a short time -- not choosing -- although it does not obtain but processings of a low-temperature long time are short time, such as need or laser heating, -- a throughput -- smallness --

there was a fault of the need in processing -- in addition, the particle size obtained was also as small as about 10 microns, and that of the efficiency of the produced solar battery was dissatisfied
[0008] Moreover, when the substrate which consists of the quality of the materials which have resistance also in heat treatment of comparatively an elevated-temperature long time, such as carbon and a refractory metal, was chosen, in addition to the substrate itself being expensive, property degradation by the impurity diffusion from the substrate circumference accompanying heat treatment had become a problem.
[0009] The purpose of this invention has the amount of the silicon used in offering the method that the thin film solar cell which has a few and fixed photoelectric conversion efficiency can be manufactured cheaply.
[0010]
[Means for Solving the Problem] The outline process of this invention method is explained using drawing 1 .
[0011] The ingot or wafer (it is hereafter called Si substrate.) of a polycrystal with which a single crystal or particle size becomes size remarkably By performing moderate heat treatment, after pouring the hydrogen (H) ion 2 into this (drawing 1 (a)) and pasting up the 2nd substrate 3 on the Si substrate 1 (drawing 1 (b)) The thin film Si crystal 4 of desired thickness is made to exfoliate from the Si substrate 1 (drawing 1 (c)), and this is offered as a main material which constitutes a solar battery element, or its part. In addition, not only H but the combined use of helium (helium), or H and helium of the ion kind to pour in was effective.
[0012] In order to obtain the thickness 7 microns or more (about 10 microns is more desirable) required of a thin film Si from the property of a sunlight spectrum, in this invention, two kinds of methods shown in the following (a) and (b) are proposed.
[0013] (a) Gain directly the thin film Si crystal which has thickness 7 microns or more required for a solar battery element by ablation. In H, the ion implantation in this case needs to carry out with the energy of 600 (except for the case of channeling pouring mentioned later) or more keVs, and when it is helium, it needs to carry out with the energy of 2 or more MeVs.
[0014] (b) Consider as thickness 7 microns or more by obtaining the thin film Si crystal used as the ground of a film required for element formation by the same exfoliating method, and growing Si layer epitaxially after this ground thin film Si crystal. the ease and the standard injector (pouring energy of a maximum of 400 keV(s)) of ablation are [that the thickness as a ground thin film Si crystal considers as 0.5 microns or more and 4 microns or less] usable -- etc. -- it is desirable in a field In H, in the case of 40 (except for the case of channeling pouring explained later) or more keVs and 400 keVs or less, and helium, the pouring energy in this case needs to make it 70 or more keVs and 1.5 MeVs or less.
[0015] In any [of a more than] case, about 500 degrees C or more were suitable for heat treatment after pouring.
[0016] Si substrate after exfoliation is again used repeatedly as a start material of the aforementioned process, and can realize saving-resources-ization. In addition, the various devices of light and sake generating carrier ****** are added before and after the aforementioned process for much more improvement in solar-battery efficiency.
[0017] It is based on the method of the above (a) and the operation which results in exfoliation with the ion implantation of this invention and heat treatment is explained. Although an ion kind also explains H as an example, there is no place which is different in a fundamental effect also in helium. Moreover, except that the pouring depth differs also in the method of (b), exfoliation takes place by the same operation.
[0018] In order to make the thin film Si crystal of desirable thickness exfoliate in a solar battery from Si substrate, the acceleration energy of 600 or more keVs is needed as energy from which about 7 microns or more which is the projection range (projected rang) into Si of (1) H ion are obtained first. That is, in choosing proton ion (H+) as H ion which should be poured in, when choosing hydrogen-content child ion (H2+) according to 600keV(s), the conditions of the ion source, etc., the acceleration voltage of 1.2MeV(s) is needed. Moreover, in order to cause exfoliation with next heat treatment, the hydrogen injection rate more than the digit of 1016cm-2 is needed in general.
[0019] The injection rate for concrete exfoliation achievement changes a little with pouring energy

and heat treatment conditions. Since the mass of an element is large when using elements other than H ion as an ion kind, in order to obtain the projection range of about 7 microns or more, big pouring energy is needed. For example, in order for helium ion light subsequently to H to also obtain the projection range of 7 microns, the energy of about 2 MeV(s) is required. It is unreal to use ion kinds other than H and helium in respect of an equipment scale and cost.

[0020] Subsequently, the 2nd substrate used as the foundation which holds mechanically the thin film Si crystal after (2) exfoliations is pasted up. A conductive metallic material and sunlight receive in part at least, and if it says correctly, the transparent insulating material which a photo-electric-translation wavelength region receives in part at least, and has a translucency will be suitably chosen by the structure of the solar battery which makes the purpose the quality of the material of this 2nd substrate. Although the pasting-up method accompanied by the chemical preparation of both sides which should be pasted up is generally carried out to adhesion of the 2nd substrate, since sufficient bond strength is secured, adhesives may be used. The thermal resistance from which neither of the cases poses a problem in the case of a next exfoliation process is needed.

[0021] Then, the exfoliation process by (3) heat treatments is performed. Although the still unknown point is left behind, the detail of the mechanism in which Si results in exfoliation While poured-in H ion condenses and gasifies within Si by heating The point defect of Si generated with pouring etc. is imagined that destruction of Si crystal accompanying heating takes place near the field H exists in high concentration within Si crystal conjointly with movement becoming active by heating, and a defect exists in high concentration. Most of poured-in H ion and defects are removed from the inside of the thin film Si crystal which it exfoliated and was obtained by additional heat treatment performed this heat treatment and if needed.

[0022] Hereafter, light and a carrier are effectively shut up in a solar battery element, and the manufacture method of the thin film Si solar battery constituted combining the various processes of making efficiency increasing is explained.

[0023]

[Embodiments of the Invention]

(Form of the 1st operation) Drawing 2 is drawing explaining the form of operation of the 1st of this invention.

[0024] In drawing 2 (a), 11 is Si substrate and uses p type (100) substrate by this example. 12 is a portion which serves as a thin film Si crystal after exfoliation among the Si substrates 11, and since any portions other than 12 are not used for the element of this example but turn to reuse, it shows them with the dashed line.

[0025] 13 expresses the situation of pouring of H ion roughly, and is pouring in the so-called usual random direction. In advance of pouring, the thin oxidizing zone 14 and n type layer 15 were formed in the Si substrate 11. This oxidizing zone 14 is set to the thin film Si solar battery after completion, and plays the role of the passivation layer for the recombination prevention by the side of n electrode. A part of oxide film 14 is removed, and a joint with the electrode formed behind is prepared. Poured-in H ion exists in the position 16 neighborhood with a depth [in the Si substrate 11] of about 10 microns by high concentration.

[0026] It is ZnO from which drawing 2 (b) shows the 2nd substrate holding the thin film Si crystal 12, 17 becomes a glass plate and 18 becomes a transparent electrode. The thin film Si crystal 12 exfoliates by making a position 16 into the fracture surface by pasting up after pouring of H ion and heat-treating both the portions shown in drawing 2 (a) and drawing 2 (b).

[0027] In this example, the front face (and front face of an oxide film 14) of the thin film Si crystal 12 was hydrophilicity-ized by chemical preparation before adhesion, and it was able to paste up, without using adhesives in adhesion with a transparent electrode 18.

[0028] Drawing 2 (c) explains after exfoliation signs that the solar battery was constituted through various processes. as a concrete process -- additional heat treatment after (i) exfoliation (this chose the rapid heating processing (Rapid Thermal Annealing) with few heat damages to the 2nd substrate), the oxide-film 19 formation for (ii) p electrode side passivation, p (iii) electrode 20 formation, and (iv) p+ field 21 formation -- since -- it becomes

[0029] By these heat histories in process, a transparent electrode 18 and the thin film Si crystal 12 are welded as shown in drawing 2 (c), and they serve as useful n lateral electrode.

[0030] In addition, since the oxidization and diffusion in this example used the remains defect accompanying pouring positively, in low temperature, the desired property was attained from usual. Moreover, in the solar battery element in this example, incidence of the sunlight 22 is carried out from a glass-plate 17 side.
[0031] In addition, it is light to carry out etching processing of the front face of the thin film Si crystal 12 after exfoliation with an alkali solution etc. in this example.
[0032] (Form of the 2nd operation) Drawing 3 is drawing explaining the form of operation of the 2nd of this invention.
[0033] Although drawing 3 (a) is the same as that of drawing 2 (a) of the form of the 1st operation almost, in this example, etching processing of the front face of the Si substrate 11 by which repeat use is carried out is carried out with an alkali solution etc. before an ion implantation, and useful pyramid structure is formed in optical confinement. Therefore, the oxide film 14 in drawing 2 and the fracture surface 16 also serve as a configuration respectively like oxide-film 14a and fracture surface 16a. In this example, since fracture surface 16a also becomes pyramid structure, the pyramid structure on the front face of pouring in reuse is held. In addition, n type layer formation before pouring like the form of the 1st operation is not performed.
[0034] Drawing 3 (b) shows the 2nd substrate holding the thin film Si crystal 12, and 31 is an aluminum (aluminum) board and the indium (In) for which 32 was used as adhesives. The In layer 32 also has a role of a p electrode. After adhesion and exfoliation were performed like the case of the form of the 1st operation, a solar battery like drawing 3 (c) was produced.
[0035] As shown in drawing 3 (c), while welding the In layer 32 in accordance with the pyramid configuration with heat treatment, in the thin film Si crystal 12, it was spread as a sign 33 showed, and p+ field was formed, and the oxide film 19, the n+ layer 34, and the n electrode 20 were formed further one by one.
[0036] In order to carry out incidence of the light 22 from the upper surface in this example, the n electrode 20 was formed in the part on the thin film Si layer 12 like illustration. Since more effective optical confinement is planned, it is also possible to take a periodic special structure according to the FOTORISO process which used the mask on the occasion of the pyramid formation shown in drawing 3 (a) (M. A.Green et al., Proceedings of the 13 thEuropean Photovoltaic Solar Energy Conference, 1995, pp.13 -16 reference).
[0037] (Form of the 3rd operation) Drawing 4 is drawing explaining the form of operation of the 3rd of this invention.
[0038] In drawing 4 (a), 41 is Si substrate and uses p type (111) substrate by this example. After forming about 10nm thin oxide film 42, H ion implantation was performed. 43 expresses the situation of pouring of H ion roughly, and carried out not pouring of a random direction but the so-called channeling pouring in alignment with the shaft (111) in this example. If channeling pouring is performed, since the energy loss of a under [the crystal of pouring ion] is relatively small, compared with pouring of a random direction, an equivalent range can be attained with small pouring energy.
[0039] In this example, H ion reached a depth of about 10 microns also with small pouring energy compared with the form of 350keV, and the 1st and the 2nd operation. Although it was dependent also on the parallelism (precision) of channeling, in the pouring energy of 300 or more keVs, an H ion penetration depth of 10 microns or more was obtained in general.
[0040] In addition, although the ion implantation was performed through the oxide film 42 of amorphous nature, since thickness was very thin, it was convenient in the effect of channeling. Moreover, the same effect was acquired also in arrangement of the so-called field channeling parallel not only to the so-called shaft channeling but a field (110) parallel to the shaft (111) which gave [aforementioned] explanation as the method of channeling.
[0041] Generally, since Si crystal has a field (111) in a cleavage plane, when the fracture surface is (111), heat and mechanical energy until it results in fracture are small, and it ends and is better [crystal / the flat nature of the fracture surface] than the case where other fields turn into the fracture surface. In this example, it resulted in fracture with low-temperature heat treatment comparatively with 380 degrees C.
[0042] Although drawing 4 (b) shows the 2nd substrate holding the thin film Si crystal 44 and

thermal resistance is inferior in 45, cheap blue sheet glass and 46 are the alloy layers of aluminum and Si used as p electrode. After adhesion and exfoliation were performed like the case of the form of the 1st and the 2nd operation, a solar battery like drawing 4 (c) was produced.
[0043] As shown in drawing 4 (c), the oxide film 42 was removed in part with heat treatment, aluminum was spread as a sign 47 showed in the thin film Si crystal 44, and it formed p+ field, and the aluminum-Si layer 46 formed the oxide film 19, the n+ layer 48, and the n electrode 20 one by one further while welding it in the portion which the thin film Si crystal 44 has exposed.
[0044] Also in this example, in order to carry out incidence of the sunlight 22 from the upper surface, the n electrode 20 formed in the part on the thin film Si layer 44 like illustration.
[0045] (Form of the 4th operation) Drawing 5 is drawing explaining the form of operation of the 4th of this invention.
[0046] In drawing 5 (a), 51 is Si substrate and uses p type (100) substrate by this example. 52 is a portion which serves as a ground thin film Si crystal after exfoliation, and except 52, since the portion of ** is not used for the element of this example but turns to reuse, it expresses it as the dashed line.
[0047] 13 expresses the situation of pouring of H ion roughly, and is pouring in the so-called usual random direction. The n+ layer 53 was formed in the Si substrate 51 in advance of pouring. Poured-in H ion exists in the position 54 neighborhood with a depth [in the Si substrate 51] of about 3 microns by high concentration. In this example, the pouring depth is shallow as compared with the case of the form of the 1st or the 3rd operation.
[0048] Drawing 5 (b) shows the 2nd substrate holding the ground thin film Si crystal 52, and 55 is a metal plate which makes iron a principal component. The ground thin film Si crystal 52 exfoliates by making a position 54 into the fracture surface by pasting up after pouring of H ion and heat-treating both the portions shown in drawing 5 (a) and drawing 5 (b). In this example, as shown in drawing 5 (c), the insulating adhesives 56 were used in adhesion.
[0049] Drawing 5 (c) explains after exfoliation signs that the solar battery was constituted through various processes. It consists of the growth of the Si epitaxial crystals 61, 62, and 63 by (i) chemical vapor-growth (CVD) method, (ii) antireflection film 64 formation, punching for electrodes (iii), (iv) embedding n electrode 65 formation, (v) embedding p electrode 66 formation, and formation of the diffusion fields 67 and 68 of the circumference of the (vi) electrode as a concrete process.
[0050] CVD was performed at lower temperature (about 600 degrees C) in consideration of the thermal resistance of a substrate and the charge of a binder, and n type layer 61, p type layer 62, and n+ type layer 63 grew one by one. Thickness could be 10 microns in the sum total from n+ type layer 53 to n+ type layer 63.
[0051] Subsequently, the antireflection film 64 for stopping the light reflex in a front face was formed. After drilling for electrodes was performed by the FOTORISO process, the n electrode 65 and the p electrode 66 were formed one by one. A reactant spatter and plating were applied to embedding formation.
[0052] Then, the component contained in the electrode with heat treatment was spread in the circumference of an electrode, and n+ type field 67 and p+ type layer 68 were formed, respectively. As for sunlight 22, incidence also of the case of this example is carried out from the upper surface.
[0053] In this example, since the electron and electron hole generated by light by pn junction being a multilayer are easily given to adjoining junction, even when a problem is in the quality of Si crystal, high efficiency is acquired as compared with structure with common (it is got blocked, and even when minority carrier diffusion length is small, it is) others. In the heat history (about a maximum of 600 degrees C) received at the time of the ablation in this example, and CVD growth, although it did not fully come to recover the defect by pouring of H ion in many cases and the minority carrier diffusion length of each class was small, sufficient solar-battery efficiency was realizable by taking the structure shown in drawing 5 (c).
[0054]
[Effect of the Invention] As explained above, according to this invention, by the conventional method of [1] mentioned above, the polycrystal Si thin film which consists of a single crystal which is not obtained, and which is not obtained by the conventional method of [2] while being able to gain more preferably 7 microns or more of thin film Si crystals of about 10-micron thickness easily, or a

diameter of a large drop about several cm or more can be gained. In the thin film of such a single crystal (or polycrystal of the diameter of a large drop of the grade which you may consider is a single crystal), since there is no degradation resulting from recombination and the leakage current of the carrier in the grain boundary from which particle size had become a problem by the small conventional method of [2], the same photo electric translation as the conventional thick (about several 100 microns) Si single crystal solar battery is realizable. Moreover, after the ablation process, the ingot or wafer which remained was reusable, it is advantageous also in respect of resources saving of Si, and 60 Si single crystal solar batteries of 10-micron ** have acquired it from one standard 6 inch Si single crystal wafer.

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the thin film solar cell characterized by the bird clapper from the process which gains a thin film silicon crystal with a thickness of 7 micrometers or more on the substrate of the above 2nd by the process which performs an ion implantation to the principal plane of a silicon substrate, the process on the principal plane of this silicon substrate which pastes up the 2nd substrate in part at least, the process which heat-treats the structure which consists of the aforementioned silicon substrate and the 2nd substrate, and ablation from the aforementioned silicon substrate.
[Claim 2] The manufacture method of a thin film solar cell characterized by providing the following. The process which performs an ion implantation to the principal plane of a silicon substrate. The process on the principal plane of this silicon substrate which pastes up the 2nd substrate in part at least. The process which heat-treats the structure which consists of the aforementioned silicon substrate and the 2nd substrate. The process which adds the layer which serves as a process which gains a with a 0.5-micrometer or more thickness [thickness 4 micrometers or less] thin film silicon crystal on the substrate of the above 2nd from silicon on the aforementioned thin film silicon crystal by ablation from the aforementioned silicon substrate.
[Claim 3] The manufacture method of a thin film solar cell according to claim 1 or 2 that it passes and the ion kind to pour in is characterized by the hydrogen ion or being at least one of RIUMU ion.
[Claim 4] The manufacture method of the thin film solar cell according to claim 1 or 2 characterized by making the pouring direction of ion into a direction parallel to the crystal main shafts of this silicon substrate near the direction of a normal of the principal plane of a silicon substrate, or a direction parallel to the crystal principal plane of a silicon substrate.
[Claim 5] The manufacture method of a thin film solar cell according to claim 1 or 2 that the 2nd substrate is characterized by the bird clapper from the quality of the material which a metal or a photo-electric-translation wavelength region receives in part at least, and has a translucency.
[Claim 6] The manufacture method of the thin film solar cell according to claim 1 or 2 characterized by having the process which adds the portion of the silicon substrate which has the 1st conductivity type which has the 2nd conductivity type in part before the process which performs an ion implantation.
[Claim 7] The manufacture method of the thin film solar cell according to claim 1 characterized by having the process which adds the portion which has the 2nd conductivity type to a part of thin film silicon crystal which has the 1st conductivity type.
[Claim 8] The claim 1 characterized by having the process which **********s the principal plane of a silicon substrate and forms a concavo-convex side before the process which performs an ion implantation, or the manufacture method of a thin film solar cell according to claim 2.
[Claim 9] The claim 1 characterized by having the process which **********s the principal plane of a thin film silicon crystal, and forms a concavo-convex side, or the manufacture method of a thin film solar cell according to claim 2.

[Translation done.]